



*Institute of Paper Science and Technology
Atlanta, Georgia*

IPST Technical Paper Series Number 712

The Effect of Temperature Excursion on Sulfidation of Carbon Steel
in 1% H₂S Environment

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March 1998

Submitted to
9th International Symposium on Corrosion in the Pulp and Paper Industry
Ottawa, Ontario, Canada
May 26–29, 1998

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THE EFFECT OF TEMPERATURE EXCURSION ON SULFIDATION OF CARBON STEEL IN 1% H₂S ENVIRONMENT

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ABSTRACT

Water wall tubes in the lower furnace areas of recovery boilers are known to experience thermal excursions. Sulfidation tests with thermal excursions can result in higher corrosion rates compared to equivalent tests without thermal excursions. Scale damage depends upon scale thickness, history of exposure and spike location. Results from the present study show that even a couple of infrequent thermal excursions, which lead to scale damage, may lead to a higher corrosion rate than the isothermal tests at the higher temperature of the thermal excursion.

INTRODUCTION

Water wall tube surfaces in the kraft recovery boilers experience temperature excursions that can increase the corrosion rate in the localized areas of the recovery boiler. Occasional temperature excursions can influence the corrosion of the boiler tubes on fireside by one or a combination of the following mechanisms;

- 1 increase in diffusion-controlled reaction rates and overall sulfidation reaction rate,
- 2 microcracking of the semiprotective sulfide scale due to thermal stresses and increased reaction kinetics,
- 3 molten salt corrosion (if the molten smelt is in touch with the fireside tube).

When the temperature excursions are more than the melting point of smelt then the molten salt corrosion will increase metal wastage significantly.

Diffusion in most common sulfides (FeS, Cr₂S₃, and NiS) is generally much faster than that in corresponding oxides due to higher concentration or mobility of defects in sulfide scales [1]. As a result, sulfide scales have a greater tendency to deform plastically than the corresponding oxides. Relative coefficients of thermal expansion of the metal and the corrosion product scales are of great importance in the generation of stresses in the scale. Other important factors in developing stresses in the scale are scale thickness and geometry of the metal surface. Stresses in the scale generally increase with increase in scale thickness. Scales formed on curved surfaces have higher stresses than the scale formed on a flat surface [2]. For scales that grow at the scale/gas interface, the metal surface geometry will contribute to either compressive or tensile stresses depending on whether the curved surface is convex or concave [3]. Data on oxides show that NiO and CoO (with metal/oxide thermal expansion ratio of 1.03 and 0.93, respectively) seldom crack or spall on cooling to room temperature, while FeO and Cr₂O₃ (with 1.25 and 1.30 metal/oxide thermal expansion ratio, respectively)

spall violently [4]. Stress buildup may be relieved through cracking of the scale or detachment of the scale from the parent metal. Thermal excursions may lead to scale damage due to the thermal stresses. This effect will depend upon the composition and physical properties, as well as thickness of the scale.

Temperature excursions, as high as 600°C (infrequent, and once every 2-3 months) and for relatively short time periods (typically between few minutes to few hours), have been reported in floor tubes in the recover boilers [5]. Thermal excursions are also known to occur on the water wall tubes in the lower furnace areas. On fireside, this increase is generally attributed to the smelt spalling in the local areas. Generally, the temperature excursions in the lower furnace area are below 500°C [6]. Previous work done by Colwell and Fonder [7] on SA-210 carbon steel alloy in a 1% H₂S environment at 320°C for 20 days reported that 10 spikes to 400°C increased the weight loss 19 times compared with weight loss from 320°C isothermal test. The same result represented a 374% increase when compared with weight loss from a 400°C isothermal test. Weight gain of 9-Cr steel decreased to 15 % of the weight gain of 2-Cr steel and mild steel in oxidizing environment containing 0.3% SO₂ when thermally cycled between 200 and 430°C [8]. Results from 1.25Cr-0.5Mo steel in oxidizing environment of 0.2% SO₂ with thermal cycling between a high temperature and room temperature showed a strong dependence of corrosion rates on the higher temperature, where the corrosion rates increased abruptly by 5 times around higher temperature of 700°C [9]. Thermal cycling doubled the corrosion rate of carbon and 304 stainless steels at 371°C and 482°C, respectively, when cycled to room temperature in 0.5% H₂S-containing environment [10]. However, the magnitude of the metal loss for carbon steel in the 1% H₂S environment due to occasional thermal excursions is not completely understood. Most of the previous published work to study the effects of thermal excursion on gaseous corrosion was done where continuous cycling was introduced during a given test period [7-10]. These studies clearly demonstrate that the corrosion attack is more severe due to the thermal cycling. However, in the lower furnace of recovery boiler, thermal excursions are not continuous. The present study was aimed at establishing an effect of infrequent thermal excursions on the water wall tube corrosion from fireside. To do so, test parameters in the present work were changed to study the effects of scale damage and post excursion exposure on the overall corrosion rate.

EXPERIMENTAL WORK

SA-210 carbon steel specimens were cut from a 5-cm-OD tube and burnished according to the standard procedure described in AF&PA/95 report [7,11]. The chemical composition of SA-210 carbon steel alloy is given in Table I. The specimen dimensions were 2.5 cm x 1.8 cm x 0.5 cm. Coupons were cleaned with acetone and weighed before they were hung on a glass tree and placed in the reaction tube.

Table I. Chemical Composition of SA-210 Carbon Steel Alloy.

Element	C	Mn	Si	P	S	Fe
Weight %	0.21	0.65	0.22	0.01	0.016	Bal.

The present experiments were designed to study the effects of individual temperature excursions at different time periods during the tests on the corrosion rate of SA-210 carbon steel in a 1% H₂S environment. Dimensions of thermal excursion are shown schematically in Figure 1. Tests were carried out for 72, 162 or 312 hours with temperature spikes at different times, as listed in Tables II to IV.

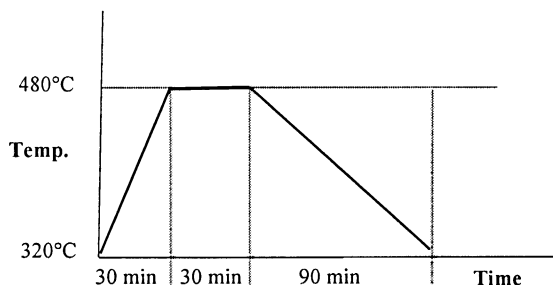


Figure 1. Schematic Diagram Showing the Dimensions of an Individual Thermal Excursion Carried Out During the Present Work.

All excursions took about 30 minutes to heat up, 30 minutes at 480°C, and then about 90 minutes to cool down to 320°C, as is shown schematically in Figure 1. That means the spike dimensions were left constant throughout the present series of tests. Some isothermal tests were also carried out at 320°C and 480°C for different time periods to get the baseline data to compare with the temperature excursion test data.

After the test was finished, specimens were taken out of the reaction tubes, sulfide scale was removed by sandblasting, and the specimens were weighed to an accuracy of 0.0001 g.

RESULTS AND DISCUSSION

Isothermal Tests

Tests were carried out for 4, 8, 24, 72, 162, and 312 hours at 320°C and 480°C to construct the baseline data with which the data from the thermal excursion tests can be compared. Results from the isothermal tests are shown in Figure 2. Weight loss from these tests shows that the weight loss increases as temperature and time increase.

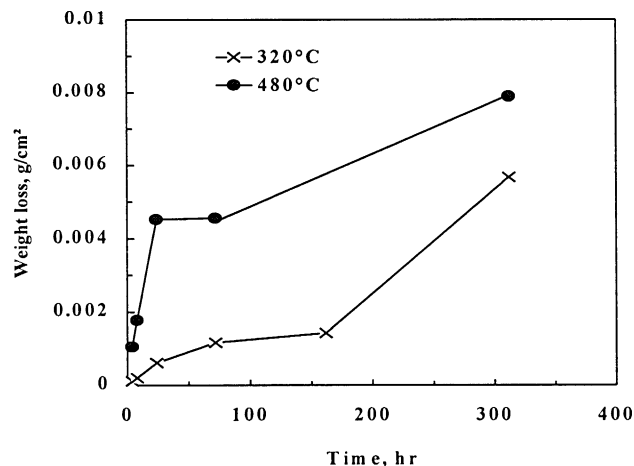


Figure 2. Weight Loss For SA-210 Carbon Steel Alloy in 1% H₂S Environment at 320°C and 480°C.

Results from 320°C isothermal tests plotted as log time vs. log weight loss indicate that the reaction follows a classical sulfidation behavior where initial corrosion rate and scale growth depend on reaction kinetics which is followed by a diffusion-controlled corrosion reaction, at a relatively lower rate. The present set of results follow diffusion-controlled scale growth until about 162 hours at 320°C. Corrosion rate increases significantly between 162 hours and 312 hours, which may be attributed to some other mechanisms, e.g. sulfide scale cracking. Results from 480°C isothermal tests give higher corrosion rates compared to 320°C.

72-hour Tests

A series of tests was carried out at 320°C for 72 hours with only one temperature spike that was either at the beginning, the middle, or the end of these tests. Weight loss of SA-210 carbon steel was higher by 92%, 81%, and 39%, respectively, as compared to the weight loss from the isothermal test carried out at 320°C. However, the weight loss for these three tests was less than the isothermal test done at 480°C. The weight loss from these tests was only 48%, 46%, and 34% respectively, of the result from the isothermal test carried out at 480°C, as is shown in Figure 3 and listed in Table III.

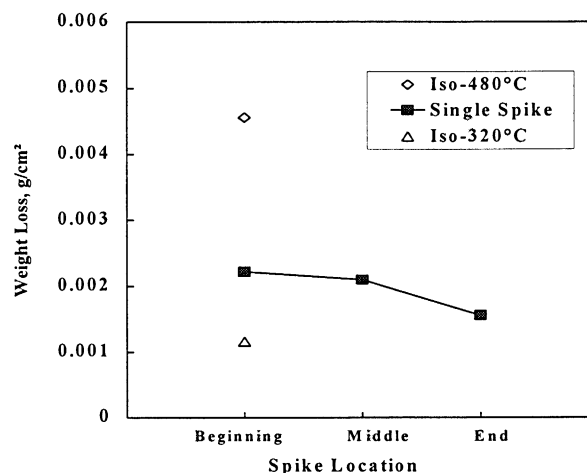


Figure 3. Weight Loss as a Function of Single Thermal Excursion Carried out During 72-hour Tests of SA-210 Carbon Steel Alloy in 1% H₂S Environment.

These results can be explained by a very simplistic model, which assumes that the temperature excursion only increases the instantaneous corrosion rate by increasing the diffusion and reaction kinetics. As is shown in Figure 4, the instantaneous corrosion rate $dC_{(Spike)}/dt_{(Spike)}$ for the spike time $dt_{(Spike)}$, is higher than the corresponding corrosion rate after the spike $dC_{(PS)}/dt_{(PS)}$ for post-spike time $dt_{(PS)}$. The corrosion rate, $dC_{(PS)}/dt_{(PS)}$, is similar to the corresponding 320°C isothermal corrosion rate at the same time period. The effect of spikes will be stronger in the beginning of scale growth and will diminish as the scale grows with time, as is shown schematically in Figure 4 and indicated by results in Figure 3.

A series of tests was carried out with two spikes at different times during the 72-hour tests to see if the effect of each spike is independent from the other one. Results from these tests show that the weight loss is higher for the tests with

two spikes compared to corresponding spikes at single location, as is shown in Figure 5. The trend for the double

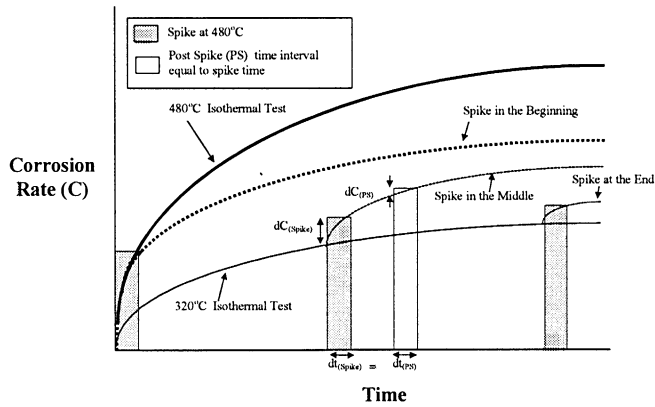


Figure 4. Simplistic Diagram Showing the Effect of Spike Location on Sulfidation Rate.

spike tests was similar to the single spike tests, in a sense that, in general, the spikes in the beginning of the tests had a larger effect on the spikes at a later time. That shows that thermal excursion depends on the history of the scale, as well as on the spike location.

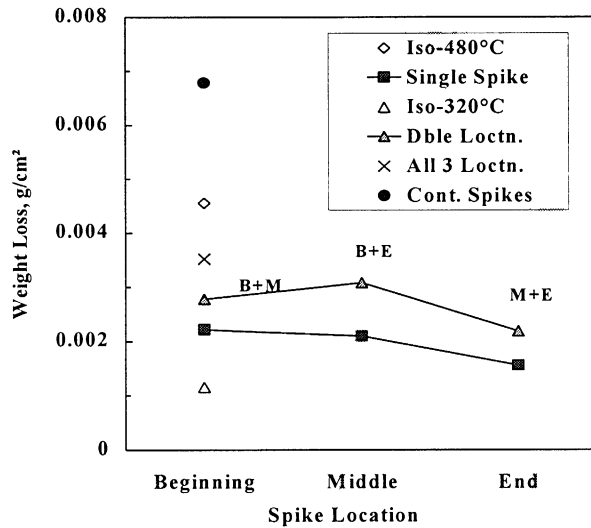


Figure 5. Weight Loss for SA-210 Specimens as a Function of Double Spike Location for 72-hour Tests in 1% H₂S Environment, Where B, M, or E, is Spike Location at The Beginning, Middle, or at The End, Respectively.

However, spike location seems to be the primary factor, since both tests associated with spike at the beginning, resulted in a higher weight loss compared to the tests carried out with spike at the end. Another test was carried out with thermal excursion in all three locations and results showed a 204% increase in weight loss compared to the isothermal test at 320°C. If we add the individual effect of each spike as shown in Figure 3 and Table II, the total effect of spikes is a 208% increase in weight loss compared to the isothermal test at 320°C. This is very close to the increase in weight loss (204%) for the test with spike in three locations, as is shown in Figure 5. This indicates that for 72-hour test time periods, the effects of spikes are additive, which may be because scale damage does not seem to participate in the overall reaction

during these tests. Scale thickness for specimens tested for 72 hours may be less than the critical scale thickness required to develop stresses that cause scale damage.

Experiment	Spike Location, Hr	Wt. Loss g/cm ² x10 ⁴ (mpy*)	%Wt Change w.r.t. 320°C	%Wt Change w.r.t. 480°C
1-iso320	0	11.6 (7)	----	----
2	1	22.2 (14)	192	49
3	34	21.0 (13)	181	46
4	69	15.6 (10)	135	34
5	1,34	27.8 (17)	240	61
6	1,69	30.8 (19)	266	68
7	34,69	21.9 (13)	189	48
8	1,34,69	35.2 (22)	304	78
9	Cont. Spikes	67.9 (41)	586	149
10-iso480	0	45.6 (28)	----	----

(*) Calculations based on the assumption that the scale is a dense layer of FeS.

Another experiment was also conducted in which thermal excursions were continuous throughout the test period. This amounted to about 23 spikes in a 72-hour test and the weight loss was about 486% more than the isothermal test at 320°C and about 150% of the isothermal test done at 480°C, as is shown in Figure 5. The results clearly show that continuous spikes may result in corrosion rates even higher than the isothermal tests carried out at the higher temperature (480°C). These results are consistent with previous work by Colwell and Fonder [7]. For 72-hour tests with frequent spikes, the location of the spikes seems to have a predominant effect on the increase in corrosion rate.

162-hour Tests

A series of tests was carried out in which a single thermal excursion was introduced at three different locations (beginning, middle, or the end) of the 162-hour test, as is shown in Table III. The weight loss increases were 305%, 514%, and 25% respectively, compared with isothermal tests carried out for 162 hours at 320°C. If we compare experiment 2 in Table II with the experiment 12 in Table III, both tests had a single spike, which starts after one hour of the beginning of the test.

Experiment	Spike Location, Hr	Wt. Loss, g/cm ² x10 ⁴ (mpy*)	%Wt Change w.r.t. 320°C	%Wt Change w.r.t. 480°C
11-iso320	0	14.2 (4)	----	----
12	1	57.7 (16)	406	----
13	80	87.2 (24)	614	----
14	159	17.7 (5)	125	----
15-iso480	0	----	----	----

(*) Calculations based on the assumption that the scale is a dense layer of FeS.

However, the test for 162 hours had much longer post spike exposure at 320°C than the 72-hour test. The effects of spike are much more significant for the 162-hour test (306% increase in weight loss compared to 320°C isothermal test) compared to the 72-hour test (92% increase in weight loss compared to 320°C isothermal test). Similarly, experiment 4 in Table II can be compared with experiment 13 in Table III. Here the tests carried out for 162 hours had a 514% increase in weight loss compared to isothermal 320°C test, whereas the test for 72 hours has only 35% weight loss increase. This illustrates an important aspect of post spike exposure. Experiment 14 in Table III was also a 162 hours test where there was almost no post spike exposure, and the weight loss was close to the corresponding isothermal test at 320°C. If a spike leads to scale damage, then the effects will be clearly demonstrated in the post spike period by a significant increase in the corrosion rate.

312-hour Tests

A series of tests was carried out in which double spikes were conducted in a 312-hour test. The location of the double spikes is shown in Figure 6. Here the location of the second spike was fixed but the location of the first spike was varied from 24 hours to 168 hours. This was done to reduce the number of variables in two-spike systems in long duration tests. The first spike location was varied to see the effects of scale history on the resultant scale damage. However, we introduced a fixed 72 hr-post spike period after the second spike to see the combined effects of double spikes, as is shown in Figure 6.

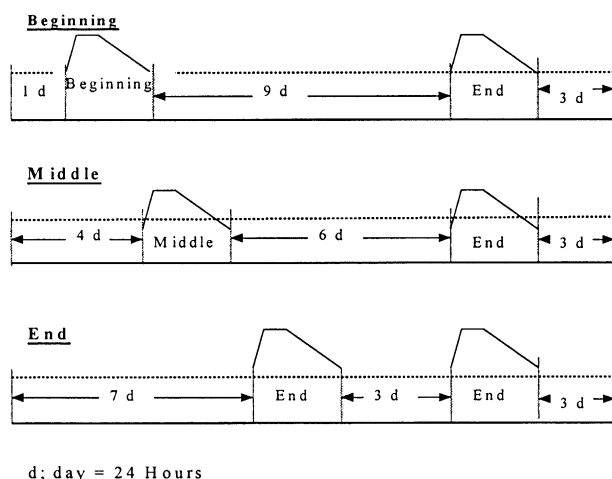


Figure 6. Schematic Diagram Showing the Double Spike Locations During 312-hour Tests in 1% H₂S Environment.

Results in Figure 7 and Table IV show that the weight loss increased by 159%, 144%, and 229% for double spikes performed at the beginning, middle and the end of the test, respectively, when compared to weight loss of the isothermal test at 320°C. It must be noted that the isothermal tests carried out at 320°C and 480°C for 312 hours have very high weight loss as is shown in Figure 2 and Table IV. For the 320°C isothermal test, weight loss was about 4 times higher for the 312-hour test compared to the 162-hour test. The same results

were 114%, 103%, and 165% when compared to weight loss of the isothermal test at 480°C, as is shown in Figure 7.

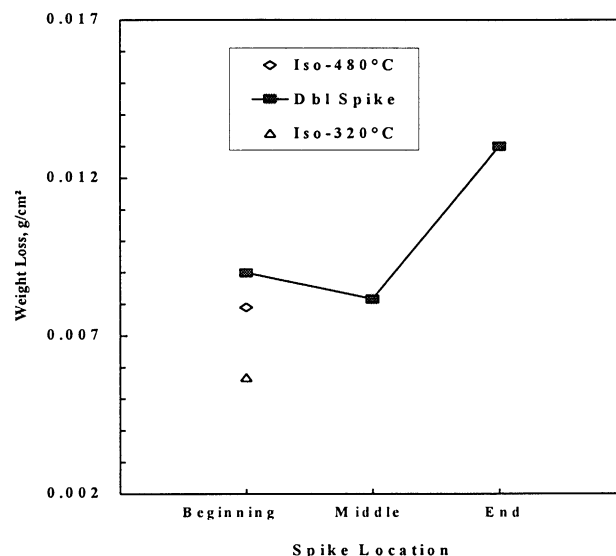


Figure 7. Weight Loss of SA-210 Specimens Due to Double Thermal Excursions Carried out During 312-hour Tests in 1% H₂S Environment.

A very important result from this series of tests is that the weight loss for all 312-hour tests with only double thermal excursions was even higher than the isothermal tests carried out at 480°C. For short test times (up to 72 hours) the scale damage does not seem to participate in the overall sulfidation mechanism and a simplistic model based on diffusion and reaction kinetics, as shown schematically in Figure 4, can explain the effects of thermal excursion. However, in long duration tests where thicker scales are more prone to scale damage due to thermal excursion and the post spike exposure effects become more predominant, the simplistic model will not explain these effects.

Experiment	Spike Location, Hr	Wt. Loss, g/cm ² x 10 ⁴ (mpy*)	%Wt Change w.r.t. 320°C	%Wt Change w.r.t. 480°C
16-iso320	0	56.7 (8)	----	----
17	24,267	89.9 (13)	159	114
18	96,267	81.6 (12)	144	103
19	168,267	130 (18)	229	165
20-iso480	0	78.9 (11)	----	----

(*) Calculations based on the assumption that the scale is a dense layer of FeS.

Results from the study also indicate that the damaged sulfide scales do not effectively heal in this system during post spike exposure. These results have a very important implication from the recovery boiler point of view that even a couple of infrequent spikes, followed by a long post spike exposure will lead to a very high corrosion rate. The corrosion of water wall tubes due to infrequent thermal spikes may even be higher than the isothermal exposure at the higher temperature of spike.

PRACTICAL IMPLICATIONS

In cases where the water wall tubes in the lower furnace areas may undergo thermal excursions, reducing the excursion amplitude and frequency may reduce the metal wastage significantly. The present work suggests that even few thermal excursions, but at higher temperature, could be very damaging. Practices that eliminate thermal excursion on the water wall tubes will reduce this type of wastage mechanism.

CONCLUSIONS

1. Thermal excursions generally leads to a higher sulfidation rate compared to equivalent tests without spikes.
2. Scale damage may depend upon scale thickness, history of exposure, and spike location.
3. A sulfide scale damaged due to thermal excursion may not heal and may lead to a very high corrosion rate in the post spike exposure.
4. Even a couple of infrequent spikes, which lead to scale damage, may lead to even higher corrosion rates than the isothermal tests at the higher temperature of the spike.

ACKNOWLEDGMENT

The authors would like to thank the DOE [Grant Number DE-FC36-95GO10092] and the AF&PA for their financial support. The authors would like to thank the members of the AF&PA's Recovery Boiler Technical Advisory Committee on Corrosion for their valuable suggestions and comments. The authors would also like to thank Mr. Douglas Singbeil of the Pulp and Paper Research Institute of Canada for providing the material.

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